Title:	Uranium and thorium detection limits of handheld Bruker Tracer III XRF spectrometer
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Uranium and thorium detection limits of handheld Bruker Tracer III XRF spectrometer

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The x-ray fluorescence (XRF) spectrometer is sensitive to the elemental composition of the assayed sample. If properly setup and tuned, the typical handheld instrument can detect x-ray fluorescence from any element usually greater than atomic number 11, i.e. from magnesium up.

Upon excitation by sufficiently energetic photons, i.e. x-rays or gamma radiation, each element emits a unique, finger-print like x-ray spectrum which can be easily recognized with a rather small probability of misidentification. When searching for traces of a particular element, the principal issue is then the signal-to-background (S/B) ratio in the energy range of peaks characteristic for the element of interest. While the signal is in general proportional to the concentration of the searched element in the sample, the background may vary greatly depending on the setting of the instrument and other elements present in the sample. The detection limit for a particular element is therefore a rather complex parameter that depends on a multitude of factors and which may vary by orders of magnitude in concentration or absolute mass.

Based on the variability of environmental conditions in places where traces of U and Th could be detected we expect the detection limit for both elements to significantly vary as well. However, in order to establish the baseline sensitivity of Bruker Tracer III under the most ideal conditions, we have performed measurements of bulk uranyl and Th solutions in thin film containers designed for XRF assay (see Fig.1) together with one of the most ideal settings of the instrument for detection of U and Th traces (i.e. 40 keV accelerating voltage, thick Al+Ti+Cu filter).

Fig. 1 *Solutions of U and Th dissolved in nitric acid with concentrations ranging from 10 to 10000 ppm. The front cups with thin polyethylene film covers contain 2-3ml of solution specifically for XRF measurements.*
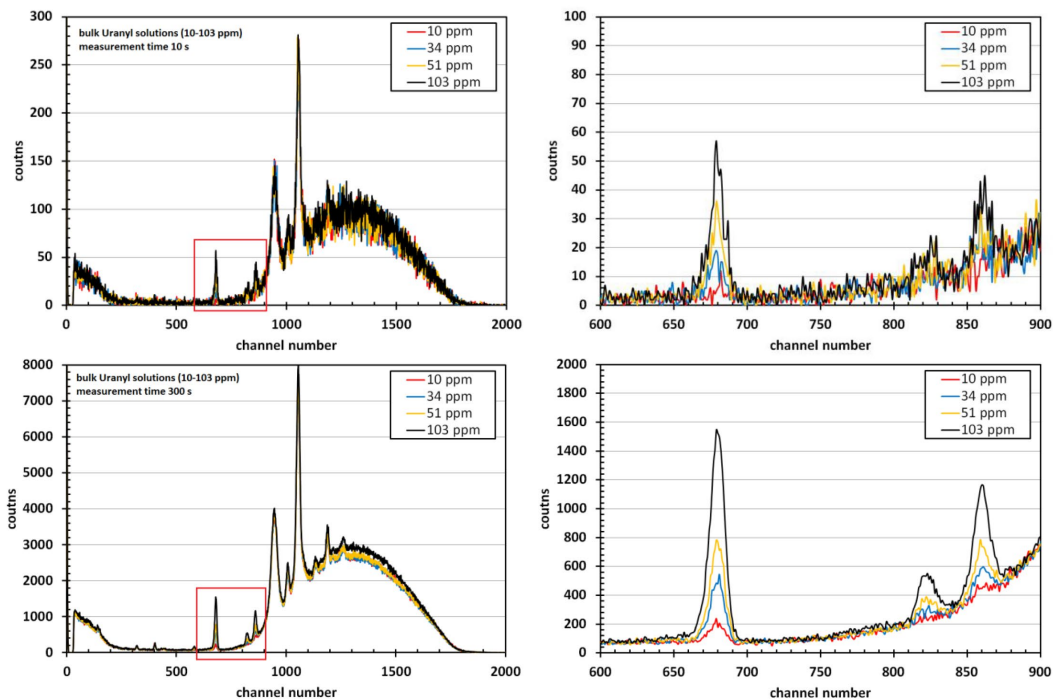
Fig.2 *XRF spectra of four uranyl solutions of different concentrations measured for 10 s (top row) and 300 s (bottom row). The red frame indicates the area of U specific peaks which are displayed in right column in greater detail.*
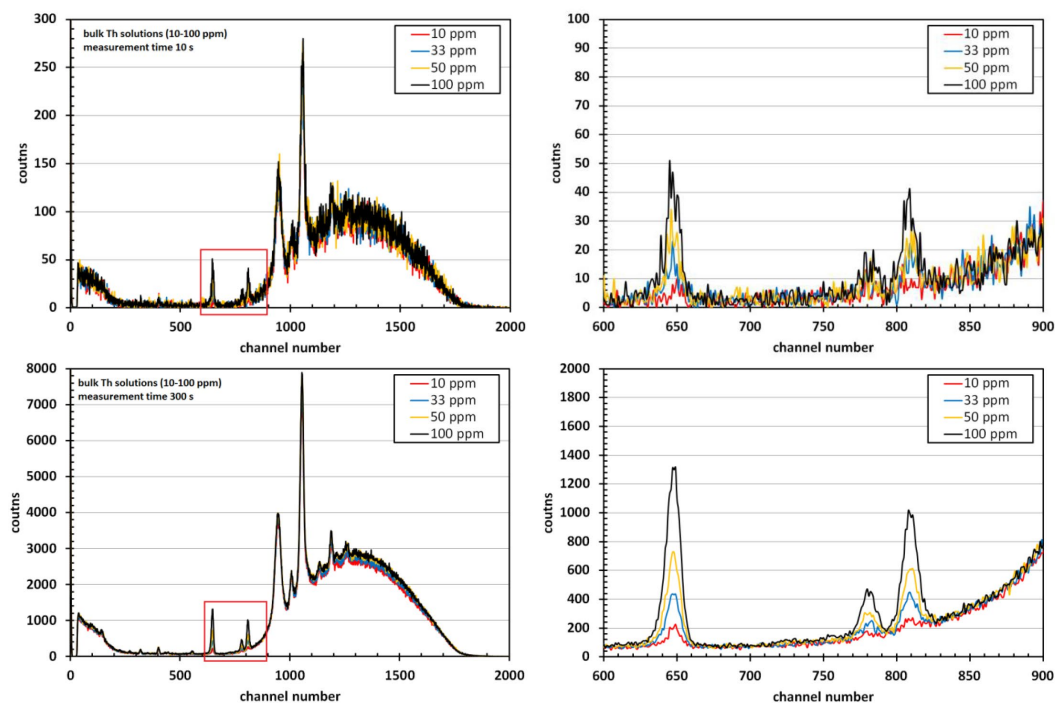
Fig.3 *XRF spectra of four Th solutions of different concentrations measured for 10 s (top row) and 300 s (bottom row). The red frame indicates the area of Th specific peaks which are displayed in right column in greater detail.*

We performed 10 s and 300 s measurements of eight samples with concentrations of U or Th being approximately 10, 33, 50, and 100 ppm. **Fig.2** displays acquired spectra of U solutions, while **Fig. 3** displays acquired spectra of Th solutions. In both figures, the left panels provide view of the entire spectrum, while the right panels zoom in on the region with relevant signature peaks of U or Th from the L_α lines.

The U and Th peaks observed in the 300 s measurements are easily identifiable, even for the lowest solution concentration of 10 ppm, but the same spectral features are nearly indistinguishable from the background in case of 10 s measurements. This is evidence for a rather anticipated conclusion that the measurement time affects the detection limits. It is also evidence of the nature of the background around the U and Th peaks which behaves statistically and is independent of the actual U and Th concentration.

In analytical chemistry, the **detection limit** (DL) is the lowest quantity of a substance that can be distinguished from the absence of that substance (a *blank value*). The detection limit is estimated from the mean of the blank, the standard deviation of the blank and some confidence factor, typically 99% (i.e. 3σ value). The DL can then be defined as 3 times standard deviation of the blank. Additionally, the **quantification limit** (QL) is typically defined as 10 times the standard deviation of the blank. For a signal at the DL, the alpha error (probability of false positive) is small (1%). However, the beta error (probability of a false negative) is 50% for a sample that has a concentration at the DL. This means a sample could contain a trace at the DL, but there is a 50% chance that a measurement would give a result less than the DL. At the QL the chance of a false negative is considered negligible.

While DL may be easily and quickly redefined for various practical purposes (e.g. 1% chance of false positive may be deemed too large for certain applications therefore the DL can be "moved" to 5σ, instead of 3σ, from the blank mean), in this work we will adhere to the standard, i.e. 3σ, definition above. In case of the measured spectra, the role of the blank is assumed by the background in the vicinity of the peaks of interest as is demonstrated in **Fig. 4**. The standard deviation of the blank is then the standard deviation of the background and we declare reaching a detection limit, if number of counts in any single channel within the energy region of interest reaches level of 3σ above the mean of the background. Both Fig. 2 and Fig. 3 show that the background does not depend on the concentration of the solution and thus for the vicinity of the U peak at 680 ch and Th peak at 650 ch, both corresponding to $L_{\alpha1}$ transitions, the background is evaluated at 0.2833 counts/s per channel. Based on this value, we may establish the detection limit for different measurement times as described in **Table 1,** and the entire functional dependence is displayed in **Fig. 5**.

Then considering the measurements of solutions of known concentration, we can calculate the maximum signal per channel that corresponds to a given concentration. Based on the measurements of 100 ppm solutions of U and Th the maximum signal rate is 4.74 cps/ch and 4.12 cps/ch, respectively. These signal rates can be renormalized for any arbitrary solution concentrations (and confirmed by measurements of actual solutions) and used for calculation of time of the measurement necessary to reach the detection limit. Examples of such are given in **Table 2**.

Table 1: *Examples of detection limits of $L_{\alpha1}$ U and Th peaks for certain measurement times.*

Measurement time [s]	Background [counts/ch]	Detection limit [counts/ch]
10	2.833	7.883
30	8.500	17.25
60	17.00	29.37
100	28.33	47.41
200	56.66	79.24
300	85.00	112.7

Table 2: *Examples of times to reach detection limit for certain concentrations of U and Th solutions.*

Concentration [ppm]	Signal Rate [cps/ch]		Time to reach DL [s]	
	U	Th	U	Th
0.1	0.00474	0.00411	113400	150800
1	0.0474	0.0411	1134	1508
5	0.237	0.206	45.35	60.00
10	0.474	0.411	11.34	15.08
50	2.37	2.06	0.453	0.600
100	4.74	4.11	0.113	0.151
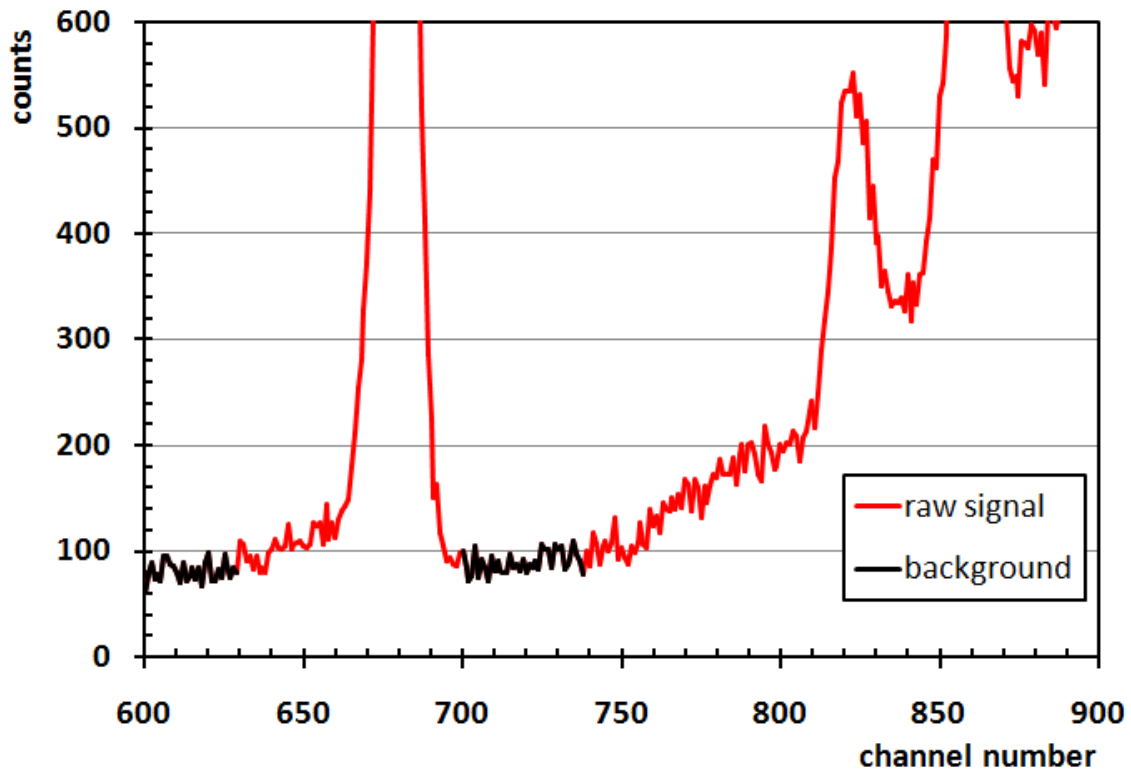
Fig.4 *Illustration of XRF signal (around 680 chn) and background for the determination of the background and signal rates. The displayed spectrum is for a 300 s measurement of 100 ppm U solution.*

Overall, the time to reach the detection limit (t_{DL}) of signal being 3σ above the background can be parameterized by a simple relation:

$$t_{DL} = \frac{9 \cdot B}{S^2}$$

where B is the background rate per channel, and S is the signal rate for a given solution concentration per channel. Based on the values of Table 2 it is possible to construct a functional dependence of t_{DL} on

solution concentration as displayed in Fig.6. This provides a formula that may be used to calculate the time required to detect any concentration of U or Th solutions in a given detector-sample configuration:

$$U: \qquad t_{DL}[s] = \frac{1134}{(w_U)^2}$$

$$Th: \qquad t_{DL}[s] = \frac{1506}{(w_{Th})^2}$$

where w is the mass fraction of the element in ppm. These formulas can be inverted and allow the calculation of the minimum detectable concentration in a fixed measurement time:

$$U: \qquad w_U[ppm] = \sqrt{\frac{1134}{t}}$$

$$Th: \qquad w_{Th}[ppm] = \sqrt{\frac{1506}{t}}$$

For example, assuming a standard 30 s measurement time (like that performed with common handheld Identifinder gamma detectors) the minimum detectable concentration of U by XRF would be about 6 ppm, and the minimum detectable concentration of Th would be around 7 ppm. (*Note: for illustration we can calculate that given the volume of the solution in these particular sample cups (~3 ml), 6-7 ppm corresponds to about 18-21 µg of U or Th. However, it should be remembered that in this case the limiting factor of the method is not the absolute amount of U or Th, but the solution concentration and the fill height of the cups.*)

To summarize this brief paper, the XRF analysis of bulk U and Th solutions provides a basis for the exploration of detection limits, the time required for the detection of known concentrations, and combinations of sample types and substrate surfaces that unique to each user's applications.
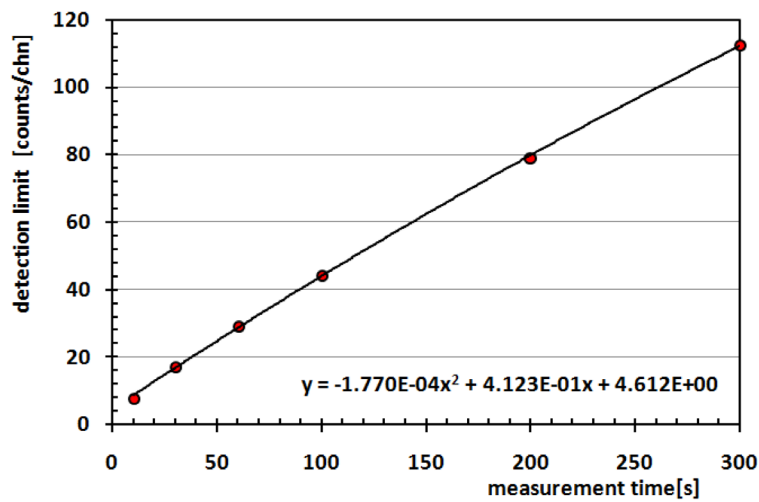
Fig. 5 XRF detection limit as a function of measurement time for bulk U and Th solutions (based on the most abundant L_α line and measurement with dedicated thin film containers).
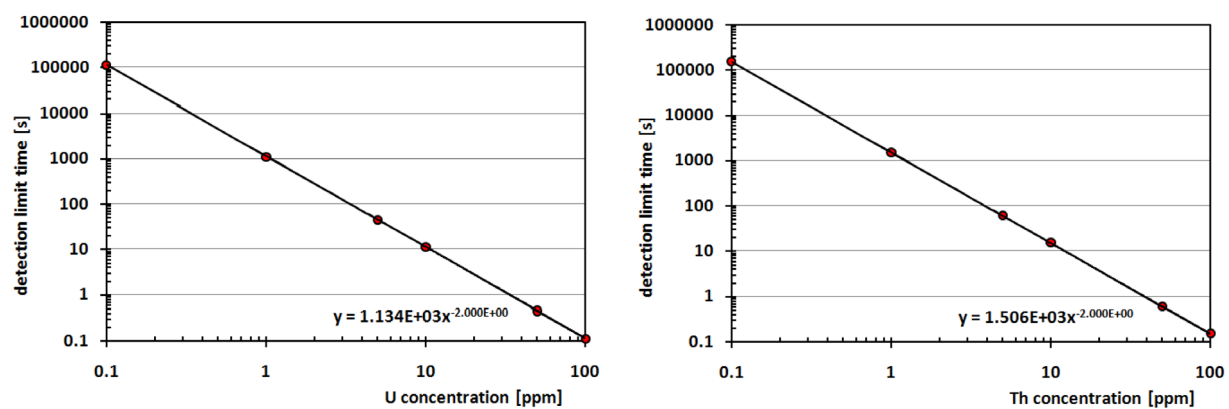
Fig.6 Dependence of t_{DL} on solution concentration for U (left) and Th (right) solutions in nitric acid.